

STRUCTURE-DYNAMIC RELATIONSHIP OF SIDE-CHAIN LIQUID CRYSTAL POLYMER WITH RIGID BACKBONE

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Abstract

To understand better the antagonistic behaviour of the backbone in comparison with the mesogenicity of the pendant side groups in side-chain liquid crystal polymers series of measurements using mechanical spectroscopy as well as DSC were carried out on two disubstituted polynorbornene derivatives.

In order to clarify the specific arrangement of chains, the influence of thermal history on the smectic phase stabilisation were studied. By quenching samples from different temperatures, it was possible to obtain the systems which were either in the glassy liquid-crystalline (LC) state or in the glassy isotropic amorphous state. The samples prepared in such ways were used to study the influence of the LC structure on the mobility of chains in amorphous regions. The quality model of the supermolecular structure of the LC polymers is proposed.

Keywords: relaxations, SCLC polymers, supermolecular structure

Introduction

The glass-rubber transition is a phenomenon which is generally observed in polymers. It not only depends on the details of the chemical structure of a macromolecule but also depends on the supermolecular structure, which is created by chains [1-5]. Moreover, the phenomenon is not restricted to polymers and is so general that one may hope to describe it by some general models. So, it seems to be very important to study the nature of the glass transition both in the academic and applied fields. A wide variety of measurement techniques, including dielectric and mechanical spectroscopy, specific heat and others, have been applied for the estimation of conformational stability of different polymers. On difficulty in understanding the glass phase lies in the definition of a glassy structure, which is not the same if we take into account variety of chemical compounds exhibiting this state. There are a lot of papers concerning the problems of glass and vitrification [6-7], and all of them indicate its one common aspect: strong structure dependency of physical parameters. It is especially important in the case of polymer which the supermolecular structures strongly influence on T_g (e.g. taken from DSC traces [1]) or α -relaxation (observed by DETA or DMTA [8]). The problem of structure-relaxation relationship in semicrystalline

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polymers was discussed earlier [9]. In this work some aspects of structure creation in liquid crystals (LC) polymers are presented. Based on new side-chain liquid crystal (SCLC) polymers with rigid backbone the relaxation processes of the glass transition zone are discussed. The quality model of the supermolecular structure for this group of polymers is presented.

Experimental

Sample preparation

The polymer samples were synthesised via ring opening metathesis polymerisation (ROMP) according to the procedure described in a previous paper [10]. This yielded a polymer with a *cis* content $s_c \approx 80$. As the racemic monomer mixture was used, the tacticity of the polymers was considered to be mainly atactic. The degree of polymerisation for the derivative CK(11), with the number of 11 methylene groups in spacer, is 478 and for the derivative CK(6) (6 methylene groups) is 355. Their chemical formula is the following: Bis[(ω -(4'-cyanobiphenyl)4-yl)oxy-*n*-alkyl]norborn-5-ene-2,3-dicarboxylate. The purified polymer was used for making the specimen for thermal analysis from melt as given in the following examples.

Polymers were melted at 160°C and were held at this temperature about 40 min in all cases. The samples were prepared between two aluminium plates. Different cooling regimes were applied from slow to very fast (quenching) one. In this way, bars with different thermal history were obtained: CK(11/III)-quenched from 140°C; CK(11/IV)-quenched from 150°C; CK(11/V)-slowly cooling; CK(11/V)_{70C/24h} slowly cooling, after that annealing at 70°C for 24 h; CK(11/VI)-quenched from 160°C; CK(11/VII)-quenched from 160°C on one Al-plate. For DSC measurements one piece of about 10 mg samples cut from those polymer bars was used.

Method

The thermoanalytical investigations were carried out with a DSC of Polymer Laboratories STA 625 type under the following conditions: environment – nitrogen atmosphere, flow rate – 50 ml min⁻¹, sample pan – aluminium, reference – empty aluminium pan, sample size – about 10 mg, heating rate – 20°C min⁻¹, calibration procedure – done with indium standard. The glass transition temperatures (T_g) were taken from the middle point of change in heat capacity. The temperatures of isotropisation (T_i) as the maximum point for each endothermal peak were pointed.

Dynamic mechanical thermal analysis was carried out with a Polymer Laboratories DMTA Mk III system. Loss tangent and E' curves were obtained in the tensile mode. A frequency range was 0.03–100 Hz and the same heating rate of measurements (0.2°C min⁻¹) within a temperature range from 10 to 80°C for CK(11) and to 105°C for CK(6) samples were applied.

Results and discussion

Disubstituted polynorbornene derivatives with the methylene units number of 11 and 6 were selected in order to observe the effect of the spacer length and the meso-

gens density per polymer unit on the macroscopic order within liquid crystal structures. Two step transitions on DSC traces were recognised earlier as the glass transitions [9]. That fact explained the shape of the T_g dependencies on the spacer lengths, which were presented in a few papers [10–12]. In opposite to the monosubstituted derivatives [11, 12], where the nematic order was only recognised, the smectic structure of both polymers with distance between layers of about 45 Å (CK(11) samples) and 35 Å (CK(6) samples) were found [13]. The structures were obtained under some specific conditions but always without external magnetic or electric field. The smectic phase was detected in samples cooled down rather slowly to room temperature or annealed at 70°C for about 24 h. SAXS studies of the samples, which the thermal treatment is mentioned above, led to the scattering curves showing several peaks. These peaks correspond to the periodicity of a layer structure (for details see [13]). Also, the samples obtained in that way showed the DSC trace characteristic for the polymers which the structure during heating events is destroyed. The original DSC traces of the samples taken under investigation were presented in the previous paper [9]. Some general rule for the samples quenched from different temperatures were observed. ΔC_p always decreases in the region of the second glass transition. This phenomenon disappears in the case of the samples held at room temperature, that takes place above the first T_g (the value extrapolated to zero heating rate is 18°C [9]) but below the second one (the extrapolated value is 38°C [9]). Then, above the first glass transition a wide endothermal peak is observed. The curve is similar to the curves of the very oriented materials. So, one can assumed that in the sample some arrangement of mesogens took place. Because this fact was not detected by X-ray measurements and rather distinct endotherm was not observed, one can suppose that the order was not perfect, like in crystals. The biggest melting peak was found for the derivative, with 6 methylene units in the spacer, obtained from precipitation.

The DMTA method was applied in the frequency range from 0.03 to 100 Hz and the data of the several samples (with different thermal history) for the temperature range in the vicinity of the both glass transitions is presented in Figs 1a and 1b. The recorded dynamic mechanical spectra in the studied temperature ranges ($\log E' \rightarrow f(T, \omega)$; $\tan \delta \rightarrow f(T, \omega)$) show shapes typical of the existence of many relaxation processes. It was possible to find at least three peaks on each plot of $\tan \delta \rightarrow f(T)$. The CK(11) and CK(6) samples showed no energy dissipation below the lower T_g . That indicates they are relatively stiff polymers in the condensed phase, with little or no motion. The curves of loss tangent ($\tan \delta$) vs. temperature vary a little as compared with each other, that would reflect the sample thermal history. Based on the stepwise decrease of the tensile modulus (E') and the value of the activation enthalpy, as well as the literature data [14–16], highest temperature relaxation is assigned to the motion of the mesogens about its short molecular axis (SMA). Because of space restriction, the full rotation is impossible. So, the motion should be treated as some kind of libration of the axis. The medial peak of all $\tan \delta$ plots is related to a main-chain relaxation process (α -Mc). The first part of the curves is rather reproducible and could be related to a side-chain relaxation (α -Sc). The similar interpretation is proposed for biomembranes, where some sub-transition connected with the fluidity of side chains is recorded by DSC. Of course, due to structural differences of lipid layers, as compared with SCLC polymers, the α -Mc relaxation is not detected.

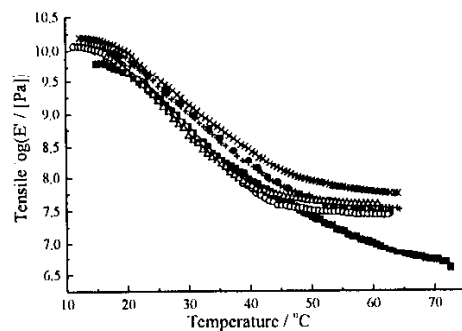


Fig. 1a DMTA data of tensile $\log E'$ of the samples CK(11) prepared under different thermal treatment. Presented curves were obtained for 3 Hz: + - CK(11/III), x - CK(11/IV), o - CK(11/V)_{70°C/24h}, • - CK(11/V), Δ - CK(11/VI), ■ - CK(11/VII)

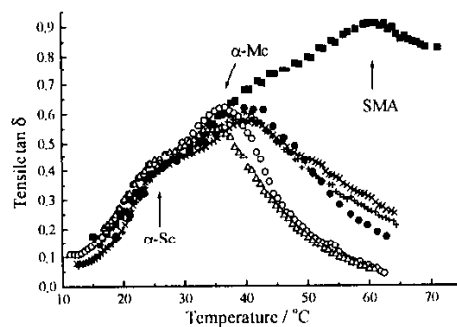


Fig. 1b DMTA data of loss tangent of the samples CK(11) prepared under different thermal treatment. Presented curves were obtained for 3 Hz: + - CK(11/III), x - CK(11/IV), o - CK(11/V)_{70°C/24h}, • - CK(11/V), Δ - CK(11/VI), ■ - CK(11/VII)

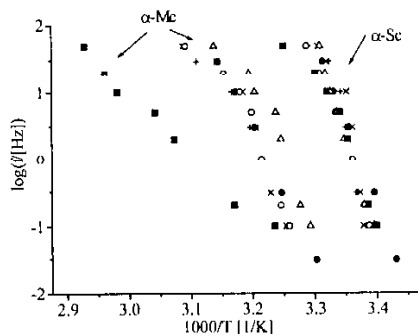


Fig. 2 Arrhenius plot of α -Sc and α -Mc relaxation for the samples CK(11) prepared under different thermal treatment: + - CK(11/III), x - CK(11/IV), o - CK(11/V)_{70°C/24h}, • - CK(11/V), Δ - CK(11/VI), ■ - CK(11/VII)

The Arrhenius plots of the α -Mc relaxations for all samples show some curvature. The same is true of the α side-chain relaxation (Fig. 2). The Arrhenius plot of the SMA relaxation of one sample (Fig. 3) shows two straight lines intersecting at definite temperature. The temperatures of each CK(11) samples, strongly depended on their preparation, are always above the second T_g value (zero heating rate extrapolation [9]). This fact would suggest that either some phase transition exist in the liquid crystal state for all samples (except for CK(6) and CK(11/VII) annealed at 110°C) or the relaxation is very sensitive to the backbone supermolecular structure. The later hypothesis would be consistent with the fact observed in the earlier SAXS study [13] and it concerns quenched samples. As one was shown, the smectic phase detected by SAXS was possible to form in the quenched samples as early as some order between the main-chains existed.

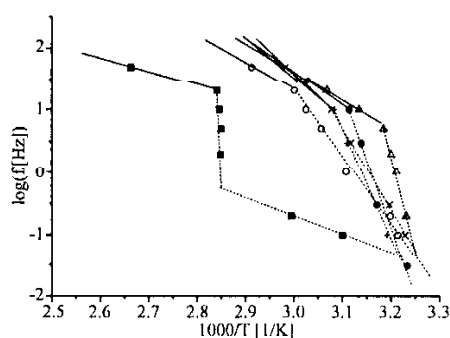


Fig. 3 Arrhenius plot of SMA relaxation for the same samples presented in Fig. 2

The Arrhenius plots of the α -Sc relaxations show the strongest curvature of all relaxations found in each sample, indicating the strongest dependency on specific volume. The lowest slope in temperature range below T_g was pointed out for the samples with different thermal treatment and they are named as CK(11/V) and CK(11/VII). The structure of the former sample was recognised as smectic A but the latter one was completely amorphous. In both cases, the fluidity of the side-chains should be the highest, although the origin of that behaviour would differ. In the smectic phase the layer spacing did not correspond to twice the length of the side chain (with mesogenic groups and CN substituent), it caused that the side chains move easier. In the completely amorphous samples quenched from isotropic state the situation concerning the side chains is quite similar but now the mesogens were fully disordered. In the nematic state the situation should differ from that of the smectic and the amorphous one, and then the side chain would be fully extended restricting its fluidity. That behaviour was observed in the cases when samples were quenched from 150 or 140°C to room temperature. The Arrhenius plot of those samples for α -Sc shows stronger curvature as compared with CK(11/V) and CK(11/VII) samples, that could prove nematic structure existence. Another reason for that behaviour is possible too, i.e. the crystallisation of the side alkyl chains. Contrary to the CK(6) polynorborene derivative, there was no evidence of a melting process of the CK(11)

samples prepared under any condition. And, a sharp endothermal peak above the first T_g was only recorded when CK(6) samples had been kept at room temperature as long as one day.

The rather low activation enthalpy for SMA process emphasises that the co-operative nature of the mesogens libration and the coupling to the backbone motions in the case of some CK(11) do not occur.

The slopes of these linear fits obey the relationship:

$$\log f_{\max} = A - H_a / (2.303RT_{\max}),$$

where R is the gas constant and H_a is the activation enthalpy of the sample phase. These values together with the thermodynamic parameters taken from DSC investigation are presented in Table 1.

Table 1 Data of the CK(11) and CK(6) samples of different thermal histories taken from DSC and DMTA measurements: T_g – temperature of the first glass transition (explanation see [9]), T_i – temperature of isotropisation, ΔH_i – enthalpy of isotropisation, H_a – enthalpy of activation of SMA relaxation, T_{inf} – the point of inflection of the line taken from Arrhenius plot (see text)

Sample	$T_g/$	$T_i/$	$\Delta H_i/$	$H_a/$	$T_{inf}/$
	$^{\circ}\text{C}$	$^{\circ}\text{C}$	kJ mol^{-1}	kJ mol^{-1}	$^{\circ}\text{C}$
CK(11/III)	23.1	149.4	7.08	125±3.6	51
CK(11/III) _{r.t.}	24.0	148.0	6.49	98.9±7.3	41
CK(11/IV)	22.8	148.0	5.25	235.9±5.3	50
CK(11/IV) _{70°C/1h}	23.1	148.0	5.63	206.0±4.3	no
CK(11/IV) _{70°C/24h}	23.8	151.3	8.62	156.9±7.5	45
CK(11/V)	25.2	150.3	6.94	93.1±2.7	45
CK(11/V) _{70°C/24h}	25.4	150.9	7.30	72.9±7.4	57
CK(11/V) _{70°C/24h} *	21.6	149.4	7.02	138.0±8.5	41
CK(11/VI)*	23.4	149.6	6.94	147.3±8.5	41
CK(11/VI) _{r.t.}	24.0	149.8	8.39	80.5±12.6	48
CK(11/VII)	20.5	149.2	8.17	no	no
CK(11/VII) _{70°C/24h}	21.5	148.7	8.58	79.1±7.9	no
CK(11/VII) _{110°C/24h}	26.0	148.9	7.03	148.5±4.8	42

no – means that the value cannot be determined

* – the sample was stored at 0°C after preparation over 48 h (see experimental section)

It is worth noticing that the activation enthalpy of the SMA relaxation increases when the samples are kept at temperature much lower than the first T_g (the example of CK(11/V)_{70°C/24h}). Now then, the α relaxation of the side-chains and/or local motions in glass state should dominate, that could disturb a little the smectic or nematic phase. As regards the annealing at 70°C during a short period of time, it would not

be enough to reorganise and to create the intermolecular order of the main-chains, which seems necessary for the smectic phase existence. In opposite to that phenomenon, the sample stored at room temperature (the temperature between both T_g s) several days show lower enthalpy. Additionally, the layer distance (d) drastically decreased [13]. Those facts would suggest that either another smectic phase had been created, e.g. smectic C, or the previous phase recognised as the smectic A had arranged better. Long time annealing at 70°C decreased the activation enthalpy in all studied cases. The samples with such a thermal treatment exhibited the smectic phase even if they were completely amorphous before annealing.

The situation looks a little different in the cases of CK(6) samples. Although, SAXS measurements showed a layer structure but the DSC studies gave very low isotropisation enthalpies [9]. Most likely, the phase transition from smectic to nematic would occur at temperature higher than 70°C (up to this temperature the SAXS measurements were performed [13]). It was pointed out from DMTA studies that the activation enthalpy of SMA relaxation of CK(6) sample is about 209 kJ mol⁻¹, that is much more as compared with the CK(11) samples. However, this would prove the strong coupling of the mesogens to backbone motions if the derivatives with the shorter spacer length is under investigation.

Microscopic observation showed that the phase situation of the polymer samples is not so clear. In some cases, the typical smectic texture together with the shirling texture, which is typical of the nematic phase, were observed. It is very important, that the condition of sample preparation in the case of microscopic observation or DSC and DMTA were different. Whereas the samples prepared to DSC and DMTA studies were submitted to the same thermal treatment and they were cut from rather thick bars (for details see [9]), the microscopic observation were performed on a very thin polymer layer cast from melt on a glass plate. The fact of different supermolecular structures of polymers should result in different motions of chains. Especially, the rotation about the short molecular axis occurred in nematic or smectic structures should be detected by DMTA in different temperature-frequency zones. So, two SMA relaxation should be detected. One results from the mesogens motion in nematic phase and another one being the consequence of the existing of the smectic phase in the sample.

It is typical of oriented polymeric structures, where the modulus of the sample is very anisotropic, that the higher values of the tensile modulus (E') should be observed. It was found in the case of CK(11/IV) as compared with CK(11/V) or CK(11/VII). This give a proof about different orientation of studied samples, which were quenched from different states (temperatures). In the case of nematic uniaxial order the dynamic E' values is highest.

In our case, perfect biaxial orientation of smectic phase induced two phase polymer. In this system some domains contain the oriented units (including mesogens and norbornene chains) together with small amount of the methylene groups and other domains contain only randomly folded side chains. The proposed supermolecular structure of SCLC polymers with the rigid backbone is presented in Fig. 4. Similarly to the structure rearrangement mentioned in the earlier papers [9, 13], in the case of CK(11), the main-chains must be located exactly into the smectic

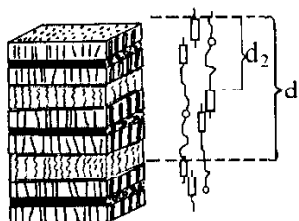


Fig. 4 Possible rearrangement of chains in a liquid crystal structure of SCLC polymers. d_1 and d_2 are the parameters determining a distance between layers in the smectic structure. The main chain, which is perpendicular with the plane, is represented by a circle. The mesogen is drawn as a rectangle and the side chain as a folded line

layers. Additionally, the main-chains should be rather ordered and create some kind of sub-layers. This would result in a layer structure with two periodicity. Of course, this supermolecular structure would self-modify with temperature. One can assume, that the smectic phase is a result of partial overlapping of the mesogens and existing of disturbed conformation of the side chains. Changes of backbone conformation should be significant and visible by DSC and DMTA due to rather big degree of polymerisation ($DP=478$) as compared with other SCLC polymers.

As a results of two regions within the system, the lower E' values are obtained and the modulus curve fall in between the curves obtained for CK(11/IV) and CH(11/VII). Although, the oriented region is expected to have a higher modulus than the unoriented one, the existence of both of them in one polymer system decreases the total value of E' . The lower one was recorded in the case of CK(11/VII), which represents pure glassy state. The effect of the methylene group substitution to the spacer on the modulus should also be observed as the consequence of different amount of the oriented and the unoriented phases. For shorter spacer higher E' value was recorded.

Conclusions

The layered structures of the SCLC polymer, with macrophase separation of the disordered and ordered domains, is postulated. The smectic phase requires a partial or total positional order of the main-chain within the LC layers and the fluidlike disordered side-chains within the neighbour layers. This results in the existence of two α -relaxation detected by DMTA. In the layered structure of these polymers the driving force for the adoption of a structure with microphase separation of the alkylene and aromatic domains is confirmed.

It is worth noticing, that the proposed quality model concerning supermolecular structure of SCLC polymers with rigid backbone well explains some physical phenomena observed by other authors and during this investigation.

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